

Appendix C

Fluorescence from Photoexcitation of Cl_2 at 50-105 nm

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Abstract

The photoabsorption and fluorescence cross sections of Cl_2 were measured in the 50-105 nm region. Excitation of Cl_2 in the 90-109 nm region emits two UV bands with peaks at 258 and 307 nm. The emission bands are attributed to the $\text{Cl}_2(\text{D}' \rightarrow \text{A}')$ transition that is produced by the energy transfer from $\text{Cl}^*(^4\text{P}_{5/2})$ to Cl_2 . The $\text{Cl}_2^+(\text{A} \rightarrow \text{X})$ emission band is produced at the excitation wavelengths shorter than 89 nm.

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1. Introduction

The quantitative absorption and fluorescence spectroscopy of Cl_2 has been investigated in the 105-145 nm region by Lee et al (1986). At 105-109 nm, fluorescence in the vacuum ultraviolet (VUV) and ultraviolet (UV) regions were observed. The dependence of the VUV emission intensity on the Cl_2 pressure is linear, but the UV band is quadratic. Recently, Nee (1988) dispersed the fluorescence produced by photoexcitation of Cl_2 with Ar resonance lines (104.8 and 106.6 nm), and he determined that the VUV emission is due to excited chlorine atoms. The UV emission is attributed to the $\text{Cl}_2(\text{D}'\text{-A}')$ and/or $\text{Cl}_2(\text{D-A})$ systems, but the assignment is not unique (Nee 1988). This paper reports a further study of the UV assignment. Intense visible fluorescence appears at the excitation wavelengths shorter than 89 nm. The emission spectra are identified to be the $\text{Cl}_2^+(\text{A } ^2\Pi_u \rightarrow \text{X } ^2\Pi_g)$ system. The potential curves calculated by Peyerimhoff and Buenker (1981) serve as an excellent guide for the interpretation of the current observation.

The absorption cross section of Cl_2 has been recently measured in the 15.5-103.8 nm region by Samson and Angel (1987) using a spark discharge light source. The data are, however, quite different from the calculated values (Carlson et al 1983, Kilcoyne et al 1987). A check of these differences is of interest.

2. Experimental

The photoabsorption and fluorescence cross sections were measured using synchrotron radiation produced by the electron storage ring at the University of Wisconsin. The experimental setup for these measurements has been described in previous papers (Lee et al 1986, 1990). Thin film windows of Al, Sn, and In were used for the measurements in the 50-60, 54-76, and 74-106 nm regions, respectively. These windows were used to separate the vacuum

monochromator from the gas cell (3.5 cm in diameter and 40.9 cm long) as well as to cut off the high-order light. The sample gas was slowly pumped by a sorption pump. The fluorescence was observed simultaneously with the absorption measurement in a direction perpendicular to the light source path.

The apparatus used for the fluorescence dispersion experiment is a modification of the one used in the earlier measurements (Judge and Lee 1972). The new apparatus has been depicted in a previous paper (Lee et al 1990). In brief, the light source was a condensed-capillary discharge lamp that was discharged by a 10 KV DC power supply pulsed by a hydrogen thyratron. The discharge medium was Ar or N₂ with a trace of O₂. The emission lines in the 45-200 nm region were selected by a 1-m vacuum monochromator for the experiments. There were no windows in the light source path. The fluorescence was dispersed by an optical multichannel analyzer with a variable time delay and gate duration.

The gas used in the synchrotron radiation experiment was supplied by Matheson with a stated purity better than 99.9%. The gas used in the fluorescence dispersion experiment was supplied by MG Industries with a stated purity better than 99.5%. The gas was used as delivered. The gas pressures used in the measurements were kept below 30 mTorr.

3. Results

3.1 Absorption and fluorescence cross sections

The absorption cross section at 50-105 nm is shown in Fig. 1(a). The experimental uncertainty is estimated to be $\pm 10\%$ of the given value. The current data are systematically lower than the measurements of Samson and Angel (1987) by about 12%. The reason for the discrepancy is not known. The current data are systematically higher than the calculated values (Carlson et

al 1983, Kilcoyne et al 1986). The comparison has been made by Samson and Angel (1987).

As shown in Fig. 1(a), vibrational progressions appear in the 86-100 nm region. The vibrational structure is caused by the Rydberg States, which are most likely converging to the $\text{Cl}_2^+(\text{A}^2\Pi_u)$ ion state of potential energy 14.0 eV (Cornford et al 1971, Potts et al 1971, Carlson et al 1983, Lonkhuyzen and Lange 1984). The two prominent progressions are very similar to the photoelectron spectrum of the $\text{Cl}_2^+(\text{A})$ state (Lonkhuyzen and Lange 1984) so that it is reasonable to assign them to the Rydberg series leading to $\text{Cl}_2^+(\text{A})$ as shown in Fig. 1(a). It is difficult to assign the leading member of each vibrational progression, because the intensity is weak. If we choose the leading vibrational levels of the two prominent progressions to be at 99.0 and 94.1 nm, their effective quantum numbers are $n^* = 3.07$ and 4.15 , corresponding to $n = 5$ and 6 , respectively. This assignment is consistent with the $n = 4$ member that has an effective quantum number of $n^* = 2.19$ as discussed in the previous paper (Lee et al 1986). The average vibrational spacings are cm^{-1} for the $n = 5$ progression and 360 cm^{-1} for $n = 6$. These spacings are close to the vibrational spacing of $\text{Cl}_2^+(\text{A})$ that is about 370 cm^{-1} (Lonkhuyzen and Lange 1984). The weak vibrational progressions in the 94-96 and 85-90 nm regions may be the Rydberg states converging to $\text{Cl}_2^+(\text{B } ^2\Sigma_g^+)$ of ionization potential 15.7 eV (Cornford et al 1971, Potts et al 1971, Carlson et al 1983, Lonkhuyzen and Lange 1984).

The cross section for the fluorescence in the 200-800 nm region is shown in Fig. 1(b). The fluorescence was observed by a photomultiplier tube (EMI 9558QB) that has a response nearly constant in the 200-400 nm region and systematically decreases toward the longer wavelength. The absolute cross

section was obtained by comparing the fluorescence intensity with that of N_2 and N_2O , for which the fluorescence cross sections are known (Lee 1977). The uncertainty is estimated to be $\pm 30\%$ of the given value. The fluorescence quantum yield which is calculated from the ratio of fluorescence cross section to absorption cross section is shown in Fig. 1(c).

For the excitation wavelengths shorter than 89 nm, the fluorescence intensity increases linearly with gas pressure so that the fluorescence cross section can be measured. But at wavelengths longer than 89 nm, the UV fluorescence intensity depends almost quadratically on the gas pressure, thus the fluorescence cross section is actually zero. The dashed curve in the 89-105 nm region in Fig. 1(b) represents an excitation function of the UV fluorescence but not the cross section. The non-linear dependence has been reported in a previous paper, and it is observed again in the current experiment. The UV fluorescence is produced by a secondary process that is subject to discussion later. The fluorescence cross section increases sharply at the threshold of the $Cl_2^+(A^2\Pi_u)$ state, indicating that the fluorescence is produced by this excited ion state. The fluorescence spectra were dispersed to identify the emission systems.

3.2 Fluorescence spectra

The fluorescence spectra produced by photoexcitation of Cl_2 at 55.1, 63.7, 68.5, 76.5, 83.4, 85.1, 86.7, 92.3, and 108.5 nm were dispersed to study the emission sources. For excitation wavelengths shorter than 88 nm, the fluorescence spectra are essentially as shown in Fig. 2 that are produced at (a) 85.1, (b) 83.4, and (c) 76.5 nm. The fluorescence is mainly in the 380-620 nm region. The emission is identified as the $Cl_2^+(A^2\Pi_u \rightarrow X^2\Pi_g)$ system. This emission system has been observed from electrical discharge of

Cl_2 (Elliott and Cameron 1937, Rao and Rao 1958, Huberman 1966) and electron excitation of Cl_2 at 350 eV (Tuckett and Peyerimhoff 1984). The emission spectrum has been extensively analyzed by Huberman (1966) and arranged into Deslandres tables by Tuckett and Peyerimhoff (1984). The vibrational numbering of $\text{Cl}_2^+(\text{A})$ was given by Lonkhuyzen and Lange (1984). The wavelength positions (Tuckett and Peyerimhoff 1984, Tuckett et al 1986) of the vibrational transitions of $\text{Cl}_2^+(\text{A } ^2\Pi_u \rightarrow \text{X } ^2\Pi_g, \Omega = \frac{1}{2} \text{ and } \frac{3}{2})$ are indicated in Fig. 2 for comparison. The spectral resolution is about 1.5 nm which is not high enough to fully resolve the vibrational bands, but the agreement for the band peak wavelengths is reasonably good.

The radiative lifetime for the $\text{Cl}_2^+(\text{A-X})$ transition was first measured by Tuckett and Peyerimhoff (1984) to be $0.41 \pm 0.03 \mu\text{s}$. The Franck-Condon weighted average lifetime is $0.54 \mu\text{s}$ (Castellucci et al 1985). The radiative lifetime was later found to be dependent on vibrational levels that vary from 0.446 to $0.593 \mu\text{s}$ (Tuckett et al 1986). This lifetime is too short to be measured accurately in the current experiment, because the pulse duration of our light source is quite long (about $1 \mu\text{s}$). Nevertheless, the radiative lifetime determined from the decay of the fluorescence intensity as a function of delay time is $0.55 \pm 0.10 \mu\text{s}$, in good agreement with the published values. This agreement tends to support that the emission is the $\text{Cl}_2^+(\text{A-X})$ system.

The fluorescence spectra produced by photoexcitation of Cl_2 at 92.3 and 108.5 nm are shown in Fig. 3. This emission is produced by a secondary process, because the pressure dependence is not linear. The UV band with a peak at 258 nm is likely the $\text{Cl}_2(\text{D}'^3\Pi_g \rightarrow \text{A}'^3\Pi_u)$ system. The $\text{Cl}_2(\text{D}'\text{-A}')$ system has been recently assigned by Tellinghuisen et al (1987, 1988), for which the spectrum is inserted in Fig. 3 for comparison. Their spectrum is much narrow-

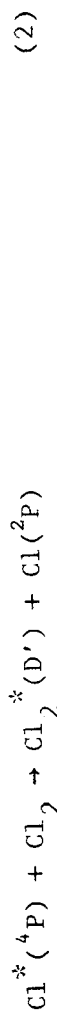
er, because it was taken at 1.35 Torr Cl_2 and 230 Torr Ar and the high vibrational levels of the upper emitting states were quenched. The sources for the band with a peak at 307 nm and the weak broad band in the 370-550 nm region are not clear, which are subject to discussion below.

4. Discussion

An excitation band for VUV emission has been observed in the 105-109 nm region by Lee et al (1986). The VUV fluorescence spectrum produced at 104.8 and 106.6 nm was dispersed by Nee (1988), which is very similar to the one published by Bemand and Clyne (1975) who observed the emission from photo-excitation of Cl_2 with a windowless He lamp that consisted of He 58.4 and H 102.6 nm lines. The emission is identified to be the $\text{Cl}(^2\text{P}, ^4\text{P} \rightarrow ^2\text{P})$ transitions in the 134-145 nm region.

The VUV fluorescence cross section (Lee et al 1986) is so high that the fluorescence is likely produced by an optically-allowed transition. According to the potential curves calculated by Peyerimhoff and Buenker (1981) as shown in Fig. 4, it is most likely that the $3^1\Pi_u (\pi \rightarrow 4s)$ state is the initial excited state. The optical excitation of Cl_2 to the $3^1\Pi_u$ state in the 11 eV region has been suggested by Spence et al (1984), and the vibrational structure of this transition in the 106-114 nm region has been assigned by Lee et al (1986). These results point to a possibility that the excited $\text{Cl}^*(^2\text{P}$ and $^4\text{P})$ atoms are produced through the $3^1\Pi_u$ state. However, this assumption contradicts the observations that: First, the excited atoms are dominated by the $\text{Cl}(^4\text{P})$ species (Bemand and Clyne 1975, Nee 1988) that can not be produced by the singlet state, and second, the threshold of the VUV fluorescence starts at 109 nm which is longer than the threshold of the $3^1\Pi_u$ dissociation limit of 106.1 nm (Lee et al 1986). These observations indicate

the excited $\text{Cl}(^4\text{P})$ atoms are not produced through the $3^1\Pi_u$ state, but by the $3^3\Pi_u$ ($\pi_u \rightarrow 4s$) state that dissociates into $\text{Cl}^*(^4\text{P}_g, 4s) + \text{Cl}(^2\text{P}_u)$ (Peyerimhoff and Buenker 1981). The threshold for this process is 108.7 nm (Bemand and Clyne 1975). The contradiction could be resolved by a proposal that Cl_2 is first excited to the $3^1\Pi_u$ state which is then predissociated through the $3^3\Pi_u$ state to produce the excited $\text{Cl}^*(^4\text{P})$. As shown in Fig. 4, the potential curve of the $3^3\Pi_u$ state is close to the $3^1\Pi_u$ state, the perturbation between these two states is likely to occur. In summary, the excitation processes involving in the energy transfer from the excited Cl^* to Cl_2 are likely:



This energy transfer process explains that the UV emission intensity depends quadratically on the gas pressure.

The decay time of the UV emission produced by the 108.5 nm excitation of 20 mTorr Cl_2 was measured to be about 1.5 μs . This decay time is much longer than the lifetime of the $\text{Cl}_2^*(\text{D}'^3\Pi_g)$ state which is only 16 ns (Moeller et al 1983). Thus, the UV decay time is not due to $\text{Cl}_2^*(\text{D}')$, but is related to the excited Cl^* atom. The decay time is so long that only the Cl^* atoms in the $^4\text{P}_{5/2}$ sublevel are possibly involving in the energy transfer. The atom in this sublevel has a transition rate of $A = 2.3 \times 10^5 \text{ s}^{-1}$ (Wiese et al 1969). The transition rates of the other two sublevels of $\text{Cl}^*(^4\text{P}_{3/2}$ and $^4\text{P}_{1/2})$ (Wiese et al 1969) are 1.3×10^7 and $2.0 \times 10^6 \text{ s}^{-1}$, respectively, which are too fast to make the energy transfer. The possibility for the energy transfer by the excited $\text{Cl}^*(^2\text{P}_{3/2}$ and $^2\text{P}_{1/2})$ atoms, which could be produced at excitation wavelengths shorter than 106.1 and 105.4 nm, is also ruled out, because their

transition rates of 4.94×10^8 and $4.97 \times 10^8 \text{ s}^{-1}$ (Wiese et al 1969), respectively, are too fast to make the energy transfer.

The electronic excitation energy of $\text{Cl}^*(^4\text{P}_{5/2})$ is 8.92 eV (Moore 1971), which is sufficient to excite the $\text{Cl}_2(\text{D}')$ state. The D' state has a potential minimum of $T_e = 7.10 \text{ eV}$ (Tellinghuisen and Chakraborty 1987, Tellinghuisen et al 1988), which dissociates into $\text{Cl}^+(^3\text{P}_g) + \text{Cl}^-(^1\text{S}_g)$ at a dissociation limit of 11.9 eV (Peyerimhoff and Buenker 1981). The energy transfer rate constant estimated from the observed emission decay time ($\sim 1.5 \mu\text{s}$ at 20 mTorr) is about $7 \times 10^{-10} \text{ cm}^3/\text{s}$. The energy transfer almost takes place in every collision.

The emission band with peak at 307 nm shown in Fig. 3 is not yet identified. This band has been repeatedly observed in the spectra by discharge of Cl_2 (Tellinghuisen and Chakraborty 1987) and by VUV excitation of Cl_2 (Moeller et al 1983). Similar to the 258 nm band, the emission intensity of this band depends quadratically on the gas pressure. The emission decay time of this band is also similar to that of the 258 nm band. These results indicate that this emission band is likely produced by the energy transfer from the excited $\text{Cl}^*(^4\text{P}_{5/2})$ atom to Cl_2 . One possible source for this emission band is that the upper state is also the $\text{Cl}_2(\text{D}'^3\Pi_g)$ state (same as that of the 258 nm band), and the lower states are the $\text{Cl}_2(^3\Sigma_u^+)$ states of which the potential curves are shown in Fig. 4. If this is the case, then the intensity ratio of the 307 nm band to the 258 nm band should be independent of the excitation process. However, the ratios measured at 92.3 nm at varied pressures are persistently smaller than those of 108.5 nm by about 10%. This difference may be suggestive that the upper state of the 307 nm band is different from that of the 258 nm band. According to the potential curves (Peyerimhoff and

Buenker 1981) and the available excited energy of Cl^* , there are two possibilities that may emit the 307 nm band. First, $\text{Cl}^*(^4\text{P})$ may transfer energy to the $\text{Cl}_2(\text{D}'^3\Pi_g)$ state at the potential well of the shorter Cl - Cl distance which then decays to the repulsive curve of the $^3\Pi_u$ state (see the curves shown in Fig. 4). Another possibility is that the $\text{Cl}^*(^4\text{P})$ may transfer energy to the $\text{Cl}_2(^1\Delta_u)$ state which subsequently transits to $\text{Cl}_2(^1\Delta_g)$. (The $^1\Delta$ potential curves are shown in the Fig. 12 of the paper by Peyerimhoff and Buenker (1981), but not shown in Fig. 4). The energy transfer to the singlet state is a highly-forbidden process which is not likely to occur. Thus, the energy transfer to the potential well of the D' state at the shorter Cl-Cl distance is more favorable, and the 307 nm band is likely due to transition from the D' to A' states at the left-hand side potential well.

Weak emission in the visible region is also shown in Fig. 3. The emission is too weak to be observed in the synchrotron experiment (Lee et al 1986). This weak emission may be produced by the excited Cl_2^* states, but the emission system is not clear. At the excitation wavelengths shorter than 89 nm, the emission consists essentially of the $\text{Cl}_2^+(\text{A } ^2\Pi_u \rightarrow \text{X } ^2\Pi_g)$ transition only. This observation is consistent with the potential curves of the ionic states (see Fig. 4), which shows that excitation to the Frank-Condon region of the $^2\Sigma_g^+$ ionic state leads to dissociation.

The 258 nm band becomes very weak at the wavelengths shorter than 90 nm, and it disappears at wavelengths shorter than 76 nm. Since the 58.4 nm excitation does not produce the 258 nm band, it will not produce the excited $\text{Cl}^*(^4\text{P})$ atom. Thus, the VUV emission observed by Bemand and Clyne (1975) was produced by the minor H 102.6 nm line alone, but not the intense He 58.4 nm line.

5. Concluding Remarks

The absorption and fluorescence cross sections of Cl_2 are measured in the 50-105 nm region. The 258 nm emission band is produced by the process that $\text{Cl}^*(^4\text{P}_{5/2})$ transfers energy to Cl_2 to form $\text{Cl}_2(\text{D}'^3\Pi_g)$ that subsequently emits to $\text{Cl}_2^*(\text{A}'^3\Pi_u)$. The 307 nm band that accompanies the 258 nm band is also produced by energy transfer from $\text{Cl}^*(^4\text{P}_{5/2})$ to Cl_2 . The band is tentatively assigned to the transition from the left-hand side potential well of the $\text{D}'^3\Pi_g$ state to the $\text{A}'^3\Pi_u$ state. The $\text{Cl}_2^+(\text{A}'^2\Pi_u \rightarrow \text{X}'^2\Sigma_g^+)$ transition is observed at excitation wavelengths shorter than 89 nm.

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Figure Captions

- Fig. 1. (a) Absorption cross section, (b) fluorescence cross section, and (c) fluorescence quantum yield of Cl_2 . The cross section is in units of Mb (10^{-18} cm^2). The Rydberg States converging to $\text{Cl}_2^+(^2\Pi_u)$ are indicated. The fluorescence was observed in the 200-800 nm region.
- Fig. 2. Fluorescence spectra of Cl_2 produced at (a) 85.1. (b) 83.4, and (c) 76.5 nm. The wavelength positions of the vibrational transitions given by Tuckett and Peyerimhoff (1984) are indicated. The Cl_2 pressure was 20 mTorr, and the spectral resolution was 1.5 nm.
- Fig. 3. The UV fluorescence spectra produced by photoexcitation of Cl_2 at 92.3 and 108.5 nm. The spectral resolution was 6 nm. The insert is the $\text{Cl}_2(D' \rightarrow A')$ emission spectrum (Tellinghuisen and Chakraborty 1987).
- Fig. 4. Potential curves relevant to the current discussion (Peyerimhoff and Buenker 1981).

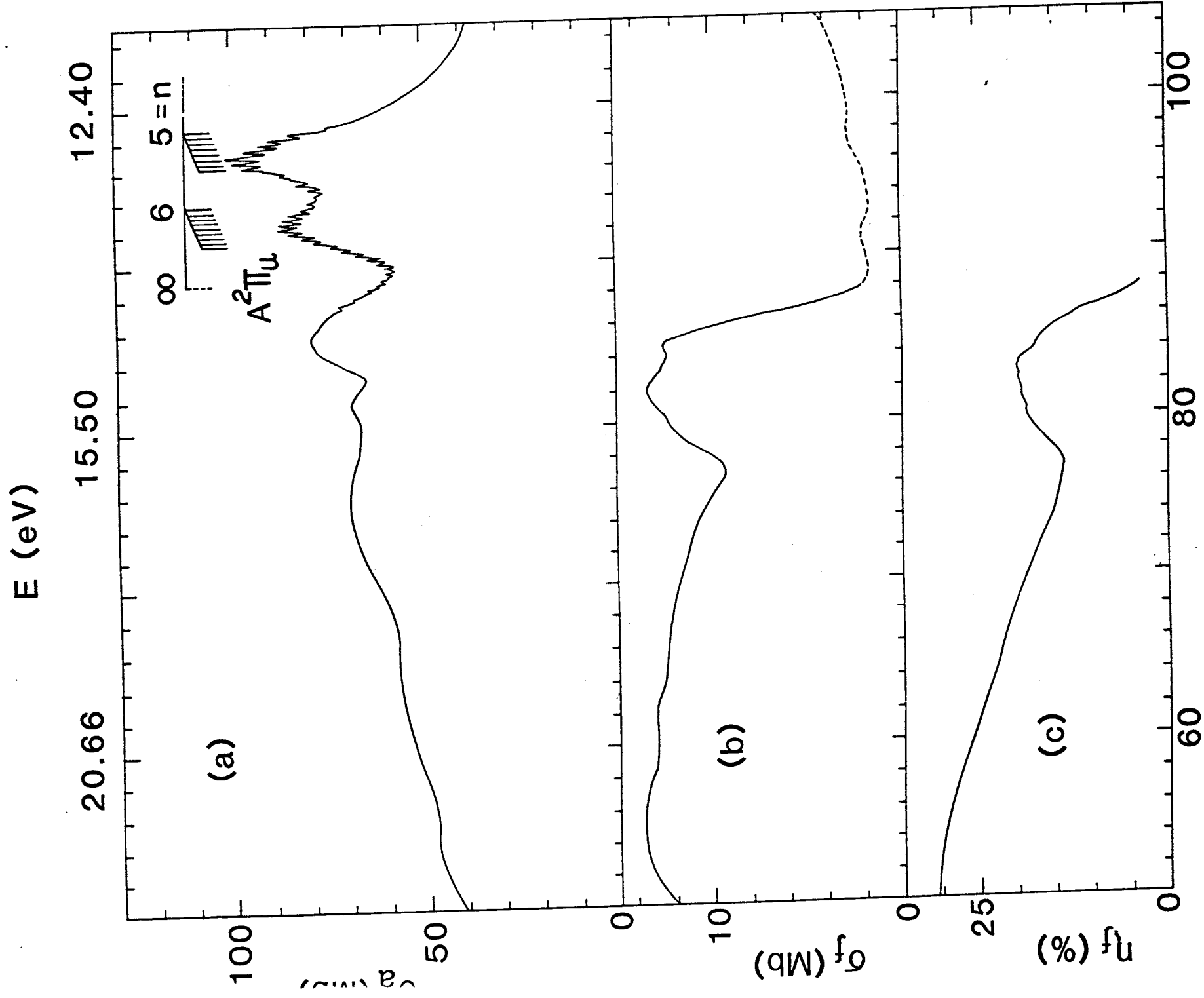


Fig. 1

Fig. 3

